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ALTERNATIVE DERIVATION OF THE
EQUATIONS GOVERNING THE FIREBALL
THERMO DYNAMICS

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GOVERNING THE FIREBALL THERMO DYNAMICS

R. N. Wilson

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ABSTRACT

In this report we present two alternate derivations of the equations governing the thermodynamics for a simple model of fireball rise and entrainment. These two derivations place emphasis on different sets of thermodynamic variables. It is shown that, except for difference in notation, the resulting equations governing the fireball thermodynamics are identical. One of the reasons for presenting the two different derivations is to clarify some of the differences and similarities of work published by various authors in this area. Unlike the work most recently published by us, there are some other treatments where terms involving the time rate of change of the specific heat ratio are neglected. We point out that these terms are as important as any of the other terms in the equations governing the fireball thermodynamics in the cases where (1) energy storage in internal degrees of freedom is significant and (2) where energy transfer via dissociation and association processes is significant.

CONTENTS

| | PAGE |
|--|------|
| ABSTRACT | iv |
| INTRODUCTION | 1 |
| REVIEW OF THE DERIVATION OF EQUATIONS GOVERNING THE THERMODYNAMICS OF THE FIREBALL | 2 |
| ALTERNATE DERIVATION OF THE THERMODYNAMICAL EQUATIONS | 7 |
| EQUIVALENCE OF THE EQUATIONS GOVERNING THE THERMODYNAMICAL BEHAVIOR OF THE FIREBALL | 11 |
| REFERENCES | 15 |

1. INTRODUCTION

In a previous report¹ we presented results of a computer code designed to calculate the rise, entrainment, and chemistry of a nuclear fireball. In that report we also presented derivations of, (1) the equations of motion of the fireball rise, (2) the equations governing the thermodynamics and (3) the equations governing the chemistry of the fireball. We also presented a description of the computer code used to integrate the coupled set of differential equations governing the rise, thermodynamics and chemistry of the fireball during its rise through the atmosphere.

In this report we shall re-derive the equations governing the thermodynamics of the fireball using a different notation. The notation used here is complementary to the notation used in Reference 1 in the sense that the two notations tend to place emphasis on different physical quantities in somewhat the same way as do the different sets of thermodynamic variables in ordinary thermodynamics, which sets are related to one another by various Legendre transformations.

In Section 2 we review the derivation of the thermodynamic equations given in Reference 1, in order to make clear the premises on which that derivation was based. In Section 3 we present an analogous derivation based on another thermodynamic notation which is that often used in the description of high temperature air in equilibrium². This type of notation has been used by various authors^{3,4,5} in fireball calculations.* In Section 4 we shall show that the equations derived in Sections 2 and 3 are identical except for notation. In Section 4 we also present some concluding remarks.

* References 3, 4, and 5 are meant to be typical, not exhaustive.

2. REVIEW OF THE DERIVATION OF EQUATIONS GOVERNING THE THERMODYNAMICS OF THE FIREBALL

In Reference 1 we presented a derivation of the equations governing the thermodynamics of the fireball. This derivation was based on several premises regarding the behavior of the fireball gas during entrainment of cold air from the surrounding ambient atmosphere.

The first premise is that the fireball gas is in kinetic equilibrium although not, in general, in chemical equilibrium.

The second premise is that the pressure contributions of the various chemical species is additive, i.e., that Dalton's law of partial pressures is valid.

The third premise is that the contributions to the internal energy of the fireball gas from each of the chemical species is additive.

The fourth premise is that the equations governing the thermodynamics of the fireball during rise and entrainment, can be derived by consideration of two infinitesimal processes. The first infinitesimal process is the mixing of an increment of ambient air with the fireball at constant pressure. The second infinitesimal process is an adiabatic expansion of the fireball.

The first, second, and third premises allow us to express the pressure and internal energy (referred to unit volume) of the fireball gas and the ambient atmosphere in the form

$$p = \sum_i n_i kT, \quad E_f = \sum_i n_i [f_i(T) + C_i] \quad (2.1)$$

$$p = \sum_j n_j kT_a, \quad E_a = \sum_j n_j [f_j(T_a) + C_j] \quad (2.2)$$

In Eqs. (2.1) and (2.2) the sum over i is a sum over the many chemical species of the fireball while the sum over j is a sum over the few chemical species of the surrounding ambient atmosphere. n_i denotes the number density (concentration) of the i^{th} species, T the fireball (kinetic) temperature, T_a the temperature of the ambient atmosphere, k Boltzmann's constant, $f_i(T)$ the temperature dependence of the internal energy contribution of the i^{th} species and C_i the heat of formation of the i^{th} species.

In Eqs. (2.1) and (2.2) the pressures of the fireball and the ambient atmosphere are the same, corresponding to pressure equilibrium of the fireball with the ambient atmosphere.

In Reference 1 we combined the two infinitesimal processes mentioned above and derived the equations which govern the thermodynamics of the fireball. To avoid any confusion that might arise in the reader's mind about the effects arising from each of the processes we shall here consider each process separately and show that the same results are obtained.

We first consider the process of mixing at constant pressure a mass ΔM of ambient air with the fireball gas. We can associate a volume ΔV_a of the ambient air parcel and we have

$$\Delta V_a = \frac{\Delta M}{\rho_a} \quad (2.3)$$

where

$$\rho_a = \sum_j \mu_j n_j \quad (2.4)$$

In Eq. (2.4) ρ_a represents the density of ambient air and μ_j the molecular weight of the j^{th} species. For the constant pressure process we have

$$E_{\text{final}} = (V + \Delta V_1) \sum_i (n_i + \Delta n_i^1) [f_i(T + \Delta T_1) + C_i] \quad (2.5)$$

$$E_{\text{initial}} = V \sum_i n_i [f_i(T) + C_i] + \Delta V_a \sum_j n_j [f_j(T_a) + C_j] \quad (2.6)$$

$$V_{\text{final}} = V + \Delta V_1 \quad (2.7)$$

$$V_{\text{initial}} = V + \Delta V_a \quad (2.8)$$

In Eqs. (2.5) - (2.8), E denotes the total internal energy of the fireball, ΔV_1 the change in fireball volume, Δn_i^1 the change in species concentrations, and ΔT_1 the change in the fireball temperature. The constant pressure process is one in which no heat is added to the thermodynamic system consisting of the fireball and the ambient air parcel of mass ΔM . Thus, the first law of thermodynamics yields

$$0 = dQ = p(V_{\text{final}} - V_{\text{initial}}) + E_{\text{final}} - E_{\text{initial}} \quad (2.9)$$

We substitute the expressions (2.5) - (2.8) into Eq. (2.9) and keep through first order infinitesimals. The result is

$$\begin{aligned} \Delta V_1 [p + \sum_i n_i (f_i + C_i)] + V \sum_i \Delta n_i^1 (f_i + C_i) + V \sum_i n_i \frac{df_i}{dT} \Delta T_1 \\ = \frac{\Delta M}{\rho_a} [p + \sum_j n_j (f_j(T_a) + C_j)] \end{aligned} \quad (2.10)$$

where f_i and df_i/dT are evaluated at T . The equation of state yields

$$\Delta p_1 = 0 = \sum_i \Delta n_i^1 kT + \sum_i n_i k \Delta T_1 \quad (2.11)$$

Eqs. (2.10) and (2.11) contain the information obtained by the consideration of the infinitesimal process of mixing at constant pressure.

We now consider the second process of adiabatic expansion of the fireball. We have

$$E_{\text{final}} = (V + \Delta V_1 + \Delta V_2) \sum_i (n_i + \Delta n_i^1 + \Delta n_i^2) [f_i(T + \Delta T_1 + \Delta T_2) + C_i] \quad (2.12)$$

$$E_{\text{initial}} = (V + \Delta V_1) \sum_i (n_i + \Delta n_i^1) [f_i(T + \Delta T_1) + C_i] \quad (2.13)$$

$$V_{\text{final}} = V + \Delta V_1 + \Delta V_2 \quad (2.14)$$

$$V_{\text{initial}} = V + \Delta V_1 \quad (2.15)$$

where the subscript 2 and superscript 2 refer to the adiabatic expansion process. The first law of thermodynamics becomes, for this adiabatic process

$$0 = dQ = p(V_{\text{final}} - V_{\text{initial}}) + E_{\text{final}} - E_{\text{initial}} \quad (2.16)$$

Substituting Eqs. (2.12) - (2.15) into Eq. (2.16) and making use of Eq. (2.10), we obtain

$$\Delta V_2 [p + \sum_i n_i (f_i + C_i)] + V \sum_i \Delta n_i^2 (f_i + C_i) - V \sum_i n_i \frac{df_i}{dT} \Delta T_2 = 0 \quad (2.17)$$

The equation of state yields

$$p + \Delta p_2 = \sum_i (n_i + \Delta n_i^1 + \Delta n_i^2) k (T + \Delta T_1 + \Delta T_2) \quad (2.18)$$

or with Eq. (2.11)

$$\Delta p_2 = \sum_i \Delta n_i^2 kT + \sum_i n_i k \Delta T_2 \quad (2.19)$$

Eqs. (2.17) and (2.19) constitute the information provided by the adiabatic expansion process.

Adding Eqs. (2.11) and (2.19) and noting

$$\Delta n_i = \Delta n_i^1 + \Delta n_i^2, \quad \Delta T = \Delta T_1 + \Delta T_2 \quad (2.20)$$

we obtain the differential form of

$$p = \sum_i n_i kT \quad (2.21)$$

i.e., the equation of state. Adding Eqs. (2.10) and (2.17) and noting

$$\Delta V = \Delta V_1 + \Delta V_2, \quad (2.22)$$

the Eq. (2.4) and

$$M = V \sum_i \mu_i n_i \quad (2.23)$$

we obtain

$$\begin{aligned} 0 = & \frac{1}{V} \frac{dV}{dt} [p + \sum_i n_i (f_i + C_i)] + \sum_i \frac{dn_i}{dt} (f_i + C_i) + \sum_i n_i \frac{df_i}{dT} \frac{dT}{dt} \\ & - \frac{1}{M} \frac{dM}{dt} \left(\frac{\sum_i \mu_i n_i}{\sum_j \mu_j n_j} \right) [p + \sum_j n_j (f_j + C_j)] \end{aligned} \quad (2.24)$$

Eq. (2.24) is identical with Eq. (3-45) of Reference 1.

Eq. (2.21) and (2.24), which govern the thermodynamics of the fireball, are identical with those obtained by combining the two infinitesimal processes (as was done in the derivation given in Reference 1). Since combining the processes shortens the derivation we shall treat the problem that way in the following section.

3. ALTERNATE DERIVATION OF THE THERMODYNAMICAL EQUATIONS

In this section we shall derive the equations governing the thermodynamics of the fireball, using a different notation than that of the previous section. In this notation we write the equation of state in the form

$$pV = Z \left(\frac{M}{m_0} \right) RT = NRT \quad (3.1)$$

where Z is the number of moles of air at temperature T per mole of air at STP at sea level. V is the volume of the fireball, M the mass of the fireball, T the temperature of the fireball, R the universal gas constant, m_0 the gram-molecular-mass of STP air at sea level, and N the number of moles in the fireball. Eq.(3.1) is an equation of state for a real (as distinct from an ideal) gas and therefore the quantities Z and N are not constant but vary when dissociation and association processes occur. The gas constant is given by

$$R = AK \quad (3.2)$$

where A is Avogadro's number and k is Boltzmann's constant. The gram-molecular-mass is given by

$$m_0 = A \bar{\mu}_j \quad (3.3)$$

where $\bar{\mu}_j$ is the average molecular mass associated with STP air at sea level.

We write the internal energy of the fireball in the form

$$E = NC_V(T)T \quad (3.4)$$

where the number of moles of gas in the fireball is given by

$$N = Z \left(\frac{M}{m_0} \right) = VZ (\rho/m_0) \quad (3.5)$$

The enthalpy, H , of the fireball is written

$$H = E + pV = NC_p(T)T \quad (3.6)$$

Note that the quantities C_V and C_p of Eqs. (3.4) and (3.6) are not the specific heats per mole as they would be conventionally defined in thermodynamics. In the conventional sense,

$$C_V' = \frac{1}{N} \left(\frac{\partial E}{\partial T} \right)_V, \quad C_p' = \frac{1}{N} \left(\frac{\partial H}{\partial T} \right)_p \quad (3.7)$$

where C_V' , C_p' are the specific heats per mole.⁶ We shall find it convenient in what follows to define a quantity

$$\gamma = C_p(T)/C_V(T) \quad (3.8)$$

where C_p , C_V are defined by Eqs. (3.4) and (3.6). The conventional specific heat ratio γ' , on the other hand, is given by $\gamma' = C_p'/C_V'$.

We now consider the combined infinitesimal process of adding, at constant pressure, a parcel of ambient air of mass, ΔM , to the fireball and then expanding the fireball adiabatically. From Eq. (3.1) we obtain

$$\Delta p = \Delta Z \left(\frac{R}{m_0} \right) T \rho + Z \left(\frac{R}{m_0} \right) \Delta T \rho + Z \left(\frac{R}{m_0} \right) T \Delta \rho \quad (3.9)$$

The initial internal energy of the system consisting of the fireball and the ambient air parcel is

$$E_{\text{initial}} = N C_V(T) T + \Delta N_a C_V(T_a) T_a \quad (3.10)$$

where

$$\Delta N_a = Z_a \left(\frac{\Delta M}{m_0} \right) = Z_a \Delta V_a (\rho_a / m_0) \quad (3.11)$$

The final internal energy is

$$E_{\text{final}} = (N + \Delta N) C_V (T + \Delta T) (T + \Delta T) \quad (3.12)$$

The initial and final volumes of the system are

$$V_{\text{initial}} = V + \Delta V_a \quad (3.13)$$

$$V_{\text{final}} = V + \Delta V \quad (3.14)$$

The first law of thermodynamics for this adiabatic process is

$$0 = dQ = p(V_{\text{final}} - V_{\text{initial}}) + E_{\text{final}} - E_{\text{initial}} \quad (3.15)$$

We substitute Eqs.(3.10), (3.12), (3.13) and (3.14) into Eq.(3.15) and keep through first order in infinitesimals. The result is

$$p(\Delta V - \Delta V_a) + \Delta N C_V T + N_1 \left[\frac{dC_V}{dT} T + C_V \right] \Delta T = \Delta N_a C_V (T_a) T_a \quad (3.16)$$

Eq.(3.9) can be rewritten (using Eq.(3.1))

$$\Delta p V + p \Delta V = \Delta N R T + N R \Delta T \quad (3.17)$$

Multiplying Eq.(3.17) by $C_V(T)/R$ and subtracting the result from Eq.(3.16) we obtain

$$p(\Delta V - \Delta V_a) + \frac{C_V}{R} (\Delta p V + p \Delta V) + N \frac{dC_V}{dT} T \Delta T = \Delta N_a C_V (T_a) T_a \quad (3.18)$$

We now introduce the quantity

$$\gamma = \frac{C_V + R}{C_V} \quad (3.19)$$

and note that since $\rho = M/V$, we also have

$$\frac{\Delta V}{V} = \frac{\Delta M}{M} - \frac{\Delta \rho}{\rho} \quad (3.20)$$

With these relations, Eq. (3.11) and the relation

$$\gamma_a = \frac{C_V(T_a) + R}{C(T_a)} \quad (3.21)$$

we find that Eq. (3.18) becomes^{*}

$$\frac{1}{\rho} \frac{d\rho}{dt} = \frac{1}{\gamma} \frac{1}{p} \frac{dp}{dt} + \frac{1}{M} \frac{dM}{dt} \left\{ 1 - \left(\frac{\gamma - 1}{\gamma_a - 1} \right) \left(\frac{\gamma_a}{\gamma} \right) \frac{Z_a T_a}{2T} \right\} - \frac{1}{\gamma} \frac{d\gamma}{dt} \frac{1}{(\gamma - 1)} \quad (3.22)$$

This equation and Eq. (3.1), which we write in the form,

$$p = Z \left(\frac{R}{m_0} \right) \rho T \quad (3.23)$$

are the analogues of Eqs. (2.24) and (2.21) of the previous section.

Eqs. (3.22) and (3.23) govern the thermodynamic behavior of the fireball.

Alternate forms of Eqs. (3.22) and (3.23) can be used instead but such alternate sets of two equations for the thermodynamic behavior must be equivalent to Eqs. (3.22) and (3.23).

* Note the presence of the last term on the right hand side of Eq. (3.22) involving the time derivative of the quantity γ . As we shall see in the following section, this term is of the same size as the other terms appearing in Eq. (3.22).

4. EQUIVALENCE OF THE EQUATIONS GOVERNING THE THERMODYNAMICAL BEHAVIOR OF THE FIREBALL

In this section we shall show that the set of Eqs. (2.21) and (2.24) is identical, except for notation, with the set given by Eqs. (3.22) and (3.23). For this purpose we find it convenient to re-introduce the variables M, V in place of ρ in Eq. (3.22). From Eqs. (3.20) and (3.22) we obtain

$$0 = \frac{1}{V} \frac{dV}{dt} + \frac{1}{Y} \frac{1}{p} \frac{dp}{dt} - \frac{1}{M} \frac{dM}{dt} \left(\frac{Y-1}{Y_a-1} \right) \left(\frac{Y_a}{Y} \right) \frac{Z_a T_a}{Z T} - \frac{1}{Y} \frac{dY}{dt} \frac{1}{(Y-1)} \quad (4.1)$$

From the Eqs. (2.21), (3.1) and (3.2) we obtain

$$N = \frac{V \sum_i n_i}{A} \quad (4.2)$$

From Eqs. (2.1) and (3.4)

$$N C_V T = V \sum_i n_i (f_i(T) + C_i) \quad (4.3)$$

and substituting for N from Eq. (4.2) we get

$$C_V(T) = A \frac{\sum_i n_i (f_i + C_i)}{\sum_i n_i T} \quad (4.4)$$

From Eq. (3.1) and the analogous equation for the ambient atmosphere

$$p = Z \left(\frac{R}{m_0} \right) pT = Z_a \left(\frac{R}{m_0} \right) \rho_a T_a \quad (4.5)$$

or

$$\frac{Z_a T_a}{Z T} = \frac{\rho}{\rho_a} = \frac{\sum_i u_i n_i}{\sum_j \mu_j n_j} \quad (4.6)$$

The last form of Eq.(4.6) follows from the relation (2.4) and an analogous relation for ρ .

It is convenient to use the notation of Eqs.(2.1) and (2.2), and in the following we drop the subscript f from the internal energy per unit volume, E_f , of the fireball. The equations of state (2.21) and (3.1) are obviously identical if we make the identification (4.2). Using Eqs.(4.2), (3.3) and (3.5) we obtain

$$Z = \frac{\bar{v}_j \sum_i n_i}{\sum_i \mu_i n_i} \quad (4.7)$$

It remains to show that Eqs.(2.24) and (4.1) are identical. With the notation of Eqs.(2.1) and (2.2) we can write Eq.(2.25) in the form

$$0 = \frac{1}{V} \frac{dV}{dt} (p + E) + \frac{dE}{dt} - \frac{1}{M} \frac{dM}{dt} \frac{\rho}{\rho_a} (p + E_a) \quad (4.8)$$

From Eq.(4.4) we have

$$C_V(T) = Ak \frac{E}{p}, \quad C_p(T) = C_V + R = Ak (1 + E/p) \quad (4.9)$$

Thus

$$\gamma = \frac{p + E}{E}, \quad \gamma_a = \frac{p + E_a}{E_a} \quad (4.10)$$

and therefore

$$\frac{\gamma-1}{\gamma} = \frac{p}{p+E}, \quad \frac{\gamma_a-1}{\gamma_a} = \frac{p}{p+E_a} \quad (4.11)$$

With this notation Eq.(4.1) becomes

$$0 = \frac{1}{V} \frac{dV}{dt} + \left(\frac{E}{p+E} \right) \frac{1}{p} \frac{dp}{dt} - \frac{1}{M} \frac{dM}{dt} \frac{\rho}{\rho_a} \left(\frac{p+E_a}{p+E} \right) - \frac{\frac{dp}{dt} E - \frac{dE}{dt} p}{p(p+E)} \quad (4.12)$$

The second term on the right-hand-side is cancelled by the first member of the last term on the right-hand-side and we obtain

$$0 = \frac{1}{V} \frac{dV}{dt} + \frac{1}{(p+E)} \frac{dE}{dt} - \frac{1}{M} \frac{dM}{dt} \frac{\rho}{\rho_a} \left(\frac{p+E_a}{p+E} \right) \quad (4.13)$$

which is identical with Eq.(4.8). This concludes the demonstration of equivalence.

Finally we remark that the last term on the right-hand-side of Eq.(4.12) is, in general, of the same magnitude as the other terms in Eq.(4.12). The last term arises from the term involving dy/dt in Eq.(4.1). This term is evidently neglected in some other treatments^{4,5} of the fireball thermodynamics. The last term in Eq.(4.12) vanishes in the case of an ideal gas, where

$$p = \frac{NRT}{V}, \quad E = \frac{1}{V} NC_V T \quad (4.14)$$

and the quantities N and C_V are constant. In this case we have

$$\frac{dp}{dt} = \frac{NR}{V} \frac{dT}{dt} - \frac{NRT}{V} \frac{1}{V} \frac{dV}{dt} \quad (4.15)$$

$$\frac{dE}{dt} = \frac{NC_V}{V} \frac{dT}{dt} - \frac{NC_V}{V} \frac{1}{V} \frac{dV}{dt} \quad (4.16)$$

so that

$$\frac{dp}{dt} E - \frac{dE}{dt} p = 0 \quad (4.17)$$

The treatment presented in the previous sections assumes that the fireball and ambient atmosphere gases have two properties in common with an ideal gas. These properties are (1) that the contributions to the pressure from the various species are additive and (2) that the contributions to the internal energy from the various species are additive. From the point of view of a microscopic picture embodied in a statistical mechanics description, these assumptions about the bulk properties of the gas are tantamount to the assumptions (1) that the behavior of the gas can be characterized in terms of a temperature and (2) that at constant temperature and species concentration (i.e., when there are no chemical reactions) the interactions among unbound particles (potential energy associated with interactions) make a negligible contribution to the internal energy compared with the energy associated with the kinetic and internal degrees of freedom of the particles of which the gas is composed.

On the other hand, the treatment assumes (A) that the contribution to the internal energy from the internal degrees of freedom of the various species is important and (B) that the change in the internal energy of the gas due to changes in the species concentrations is an important effect. The kinetic energy released when recombination takes place and the kinetic energy absorbed when dissociation occurs provide important energy transfer mechanisms. Suffice it to say that the last term on the right-hand side of Eq. (4.12) makes an important contribution to both effects (A) and (B).

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- *3.
- *4.
- *5.
- 6. Landau, L., and E. Lifschitz, Statistical Physics, Pergamon Press, London (1958), § 14, Eq.(14.6) and (14.7).

* These references will be made available to qualified military or government requesters on request from RADC (OCSE), GAFB, NY 13441.